obtained in nearly quantitative conversion. The infrared spectrum of this powder had a strong band at 6.9 as well as absorption at 7.5–10 μ. Weak absorption also occurred at 5.8 μ.

A suspension of 0.3 g. of the above polymer in 15 ml. of $CFCl_2CF_2Cl$ was heated in a platinum tube at 80° for 10 min. Evaporation of solvent left a thick, colorless grease. Infrared absorption of a film occurred at 5.7–5.8 μ and in the 7.5–10-μ region. No absorption was found at 6.0–7.5 μ. The F^{19} n.m.r. spectrum showed at least nine types of fluorine, including those similar to polymer XI. Rearrangement of the bulk polyaziridine XII occurred vigorously and completely, commencing at only 40°.

HX Adducts of 2,2,3-Trifluoro-3-trifluoromethylaziridine. Equimolar amounts of hydrogen fluoride and 2,3-difluoro-2-trifluoromethyl-2H-azirine (VI) were added manometrically, 0.5 atm. of each, to a 300-ml. stainless steel cylinder at 25°. After having stood for 1 day, the contents gave an infrared spectrum containing new intense bands at 3.00 (N–H) and 6.73 μ (heterocycle), while bands characteristic of VI had disappeared; this was taken as evidence for XIV, Z = F. A small amount of isomeric azirine VII was also present.

Similar addition of hydrogen chloride to VI in place of hydrogen fluoride occurred slowly at 25° in the gas phase. After 20 hr. almost all of the starting azirine was gone, and infrared bands assignable to adduct XIV (Z = Cl) at 2.94 and 6.99 μ had appeared. No isomerization to azirine VII was apparent. Similar addition of hydrogen cyanide to VI occurred in 20 hr.; infrared bands assignable to adduct XIV (Z = CN) were found at 2.94 and 6.69 μ, while absorptions due to starting material were nearly absent. As frequently happens, no $C{\equiv}N$ band was detected.

Isomerization of Azirine VI to VII. A mixture of 1.8 g. of VI and 10 mg. of anhydrous HF was heated at 50° for 4 hr. at 33 atm. in a sealed platinum tube. There was obtained an almost quantitative conversion of VI to VII, identified by infrared. Lower conversions and polymerization frequently occurred in other experiments, due to the sensitivity of the azirines.

The Synthesis and Study of Pseudo-Aromatic Compounds. V. The Synthesis of 3,4-Benzoheptafulvene, 1,2-Benzoheptafulvene, and 8-Phenyl-1,2-benzoheptafulvene[1]

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The synthesis of 3,4-benzoheptafulvene, 1,2-benzoheptafulvene, and 8-phenyl-1,2-benzoheptafulvene are described. Analysis of their n.m.r. and infrared spectra indicates that dipolar resonance interactions are of minor importance in the ground state.

Although simple MO calculations indicate that heptafulvene should be an aromatic molecule possessing a substantial π-electron delocalization energy, more advanced calculations indicate that heptafulvene should approximate a polyolefin.[2] The synthesis of heptafulvene and derivatives substituted at the 8-position of heptafulvene has provided data which demonstrates that simple heptafulvenes do not possess characteristics associated with an aromatic system exhibiting pronounced π-electron delocalization.[3-6] However, the reactivity of heptafulvene has precluded the determination of pertinent data necessary to describe the actual π-electronic interactions within the molecule. The extreme reactivity of heptafulvene can be accounted for by assuming that it is a polyolefin in the ground state and that electrophilic attack leads to an aromatic tropenium ion intermediate.[3]

Fusion of a benzene ring to the heptafulvene ring system should both stabilize the benzoheptafulvenes and increase the polyolefinic character.[7] The relatively lower stability of the benzotropenium ion[8] with respect to the tropenium ion should lessen the tendency for the benzoheptafulvenes to undergo electrophilic attack. M.O. calculations have been done for 3,4-benzoheptafulvene[2] and 1,2-benzoheptafulvene[9] and predict charge delocalization from the ring onto the 8-position and substantial π-electron delocalization energies for both compounds. However, these same calculations also predict a pronounced alternate double- and single-bond character in the seven-membered ring. The syntheses of 2H-benz[*c*,*d*]azulene and a tetra-

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[1] Presented before the Organic Division, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 4–9, 1965.

[2] G. Berthier and B. Pullman, *Trans. Faraday Soc.*, **45**, 848 (1949); E. D. Bergmann, E. Fischer, D. Ginsberg, Y. Hrishberg, D. Lauie, M. Mayot, A. Pullman, and B. Pullman, *Bull. soc. chim. France*, **18**, 684 (1951); A. Julg, *J. chim. phys.*, **52**, 50 (1953); **59**, 257 (1962); T. Nakajima and S. Katagiri, *Bull. Chem. Soc. Jaapn*, **25**, 910 (1962).

[3] W. Von E. Doering and D. W. Wiley, *Tetrahedron*, **11**, 183 (1960).

[4] R. B. Turner, W. R. Meador, W. Von E. Doering, L. H. Knox, J. R. Mayer, and D. W. Wiley, *J. Am. Chem. Soc.*, **79**, 4127 (1957).

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[7] A. Streitwieser, Jr., "Molecular Orbital Calculations for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p. 279.

[8] D. Muche, H. Strauss, and E. Heilbronner, *Helv. Chim. Acta.*, **41**, 57 (1958).

[9] A. Streitwieser, Jr., private communication.

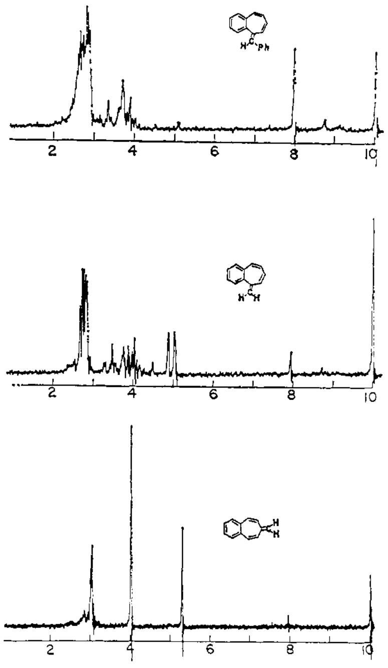

Figure 1. The n.m.r. spectra of 3,4-benzoheptafulvene, 1,2-benzoheptafulvene, and 8-phenyl-1,2-benzoheptafulvene in carbon tetrachloride using tetramethylsilane as internal standard (TMS = τ 10). The peak at τ 7.95 is due to trimethylamine.

methyl derivative have been reported, and constitute the only available data concerning the benzoheptafulvenes.[10] Because of the theoretical significance of the heptafulvene ring system and the expectation that the benzoheptafulvenes would be more tractable, while giving valuable information concerning the π-electronic interactions in heptafulvenes, the synthesis of the benzoheptafulvenes has been undertaken and is reported herein.

Several recent reports indicate that heptafulvenes can be synthesized by deprotonation of alkyl-substituted tropenium ions.[5,6,11] The approach used in this study was the synthesis of 1-methyl-4,5-benzotropenium ion and 1-methyl-2,3-benzotropenium ion and subsequent deprotonation by trimethylamine.

Addition of methylmagnesium iodide to 2,3-benzocyclohepta-2,4-dienone[12] (**1**) gave the corresponding 1-methyl-2,3-benzocyclohepta-2,4-dienol (**2**) which could be readily dehydrated with ethanolic hydrochloric acid[13] to 2-methyl-3,4-benzocycloheptatriene (**3**). Although the alcohol **2** could not be crystallized and was directly dehydrated to the benzocycloheptatriene **3**, the structure of the hydrocarbon could be readily established. Hydrogenation of this hydrocarbon resulted in an uptake of 1.84 moles of hydrogen, indicating two nonaromatic double bonds. The low value is attributable to an impurity of some 2,3-benzocyclohept-2-enone in **1** which could be detected in the n.m.r. spectrum, but could not be satisfactorily separated by v.p.c. The most satisfactory confirmation of the structure of the 2-methyl-3,4-benzocycloheptatriene (**3**) was obtained by its characteristic hydride exchange[14] with triphenylmethylcarbonium perchlorate or hexachloroantimonate to give the corresponding 1-methyl-2,3-benzotropenium ion (**4**) and triphenylmethane. The structure of the 1-methyl-2,3-benzotropenium ion (**4**) was established by its n.m.r. spectrum and the similarity of its ultraviolet spectrum to that of benzotropenium perchlorate.[15] The perchlorate salt of **4** was stable only in a nitrogen atmosphere and rapidly decomposed upon exposure to the air. However, the hexachloroantimonate salt of **4** was quite stable in the air and could be stored for long periods with no special precautions. Because the hexachloroantimonate salt was too insoluble in common organic solvents, it was not used in any subsequent step. The perchlorate salt was used to synthesize 1,2-benzoheptafulvene.

Addition of a solution of 1-methyl-2,3-benzotropenium perchlorate (**4**) in dichloromethane to a solution of trimethylamine in the same solvent caused an immediate color change. However, work-up of the reaction mixture within 1 hr. indicated little or no hydrocarbon formation. Allowing these solutions to stand for approximately 16 hr. before work-up led to an increased yield of a bright yellow hydrocarbon product. These data indicate that an intermediate ammonium salt **5** is formed which slowly decomposes to a hydrocarbon. The structure of the hydrocarbon product as 1,2-benzoheptafulvene (**6**) was verified by (i) its n.m.r. spectrum (Figure 1) which exhibited only aromatic and vinyl hydrogens, (ii) reconversion to 1-methyl-2,3-benzotropenium ion by trifluoroacetic acid, and (iii) rapid hydrogenation to 3-methyl-1,2-benzocycloheptene.

1,2-Benzoheptafulvene is indefinately stable in solution, but evaporation of the solvent from its solutions leaves an oil and results in partial decomposition as evidenced by incomplete resolution upon addition of more solvent. For this reason it was not possible to make direct weighings on the compound or determine the yield of the final step.[16] Although trifluoroacetic acid reconverted the 1,2-benzoheptafulvene to 1-methyl-2,3-benzotropenium ion in high yield, as evidenced by the n.m.r. spectrum,[17] the n.m.r. spectrum also showed the presence of a few per cent of a normal aromatic compound indicating some rearrangement during the protonation step. The rearrangement must occur during the protonation because only a single product was detected from the hydrogenation of 1,2-benzoheptafulvene. Attempts to prepare and isolate the hexachloroantimonate salt by acidification of 1,2-benzoheptafulvene were not successful.

8-Phenyl-1,2-benzoheptafulvene was prepared in a similar manner to 1,2-benzoheptafulvene. Addition of benzylmagnesium chloride to 2,3-benzocyclohepta-2,4-

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[10] V. Boekelheide and C. D. Smith, 146th National Meeting of the American Chemical Society, Denver, Colo., Jan. 1964, Abstracts, p. 34C; K. Hafner and H. Schaum, *Angew. Chem. Intern. Ed. Engl.*, **2**, 95 (1963).

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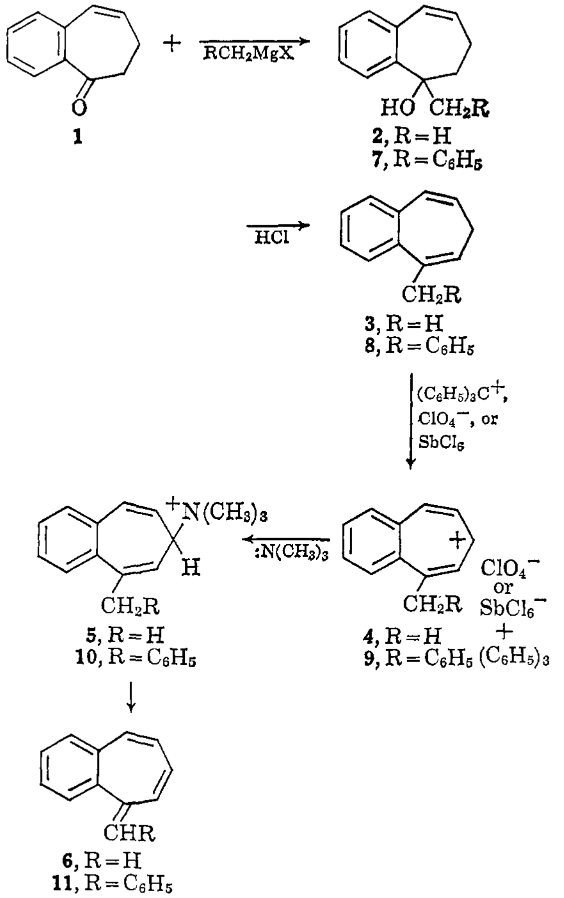
[13] L. Fieser and L. W. Newton, *J. Am. Chem. Soc.*, **64**, 917 (1942); V. Boekelheide and C. L. Larrabee, *ibid.*, **72**, 1245 (1950).

[14] H. J. Dauben, Jr., F. Gadecki, K. M. Harmon, and D. L. Pearson, *ibid.*, **79**, 4557 (1957).

[15] H. H. Rennhard, G. DiModica, W. Simon, E. Heilbronner, and A. Eschenmoser, *Helv. Chim, Acta*, **40**, 957 (1957).

[16] The yield of trimethylammonium perchlorate could not be determined because the long reaction time required caused substantial formation of a salt from the reaction of trimethylamine with dichloromethane and prohibited isolation of the trimethylammonium perchlorate.

[17] The n.m.r. spectrum clearly verified the presence of 1-methyl-2,3-benzotropenium ion because the lower field position of the tropenium ion relative to the normal aromatic by-product allowed complete resolution of the two species. The normal aromatic compound was present to an extent of approximately 10%.



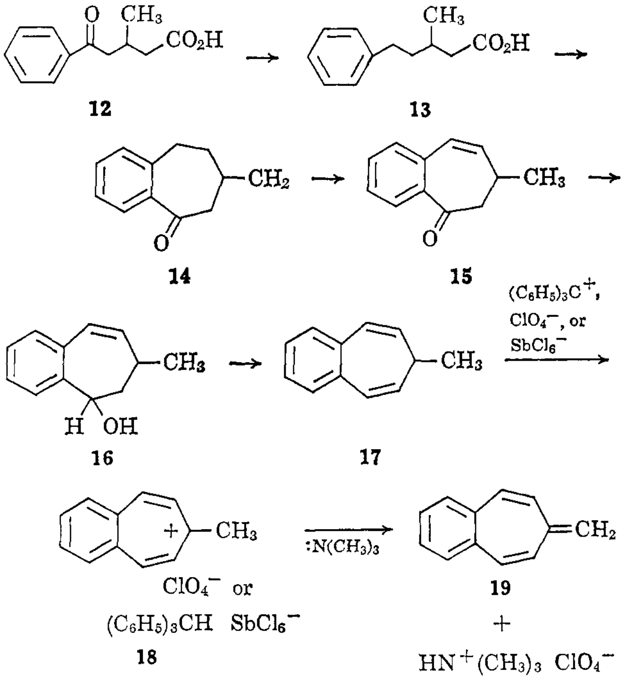
dienone (**1**) gave 1-benzyl-2,3-benzocyclohepta-2,4-dienol (**7**). This alcohol was dehydrated with ethanolic hydrochloric acid to give 2-benzyl-3,4-benzocycloheptatriene (**8**). The structure of this hydrocarbon was verified by hydrogenation which indicated an uptake of 1.80 moles of hydrogen, demonstrating the presence of two nonaromatic double bonds, and hydride exchange with triphenylmethylcarbonium perchlorate or hexachloroantimonate to give 1-benzyl-2,3-benzotropenium ion (**9**) and triphenylmethane.

The structure of the salt **9** as 1-benzyl-2,3-benzotropenium ion was verified by its n.m.r. spectrum and the similarity of its ultraviolet spectrum with that of benzotropenium perchlorate. Again, the perchlorate salt of **9** was unstable in the air while the hexachloroantimonate salt was indefinitely stable. Also, the insolubility of the hexachloroantimonate salt of **9** precluded its use in subsequent steps.

Addition of a solution of 1-benzyl-2,3-benzotropenium perchlorate in dichloromethane to a solution of excess trimethylamine in the same solvent resulted in the slow formation of a bright yellow hydrocarbon product, presumably through an intermediate ammonium salt (**10**).[16] The structure of the hydrocarbon product of this reaction as 8-phenyl-1,2-benzoheptafulvene (**11**) was demonstrated by (i) its n.m.r. spectrum (Figure 1), (ii) reconversion to 1-benzyl-2,3-benzotropenium ion by trifluoroacetic acid, and (iii) rapid hydrogenation to 3-benzyl-1,2-benzocycloheptene.

8-Phenyl-1,2-benzoheptafulvene is relatively stable and can be concentrated to an oil by a nitrogen stream, showing no decomposition within a few minutes provided the hydrocarbon is kept under nitrogen. This procedure allowed determination of the ultraviolet ε-values by direct weighing, which was not possible for 2,3-benzoheptafulvene.

The 3,4-benzoheptafulvene ring system was synthesized in a similar manner to the 2,3-benzoheptafulvene ring system. Acylation of benzene with 3-methylglutaric anhydride gave 4-benzoyl-3-methylbutyric acid (**12**) which was then reduced to 5-phenyl-3-methylpentanoic acid (**13**). Cyclization of this acid with polyphosphoric acid gave 6-methyl-2,3-benzocyclohept-2-enone (**14**). Bromination of this ketone with N-bromosuccinimide and dehydrobromination gave 6-methyl-2,3-benzocyclohepta-2,4-dienone (**15**). Reduction of this latter ketone with lithium aluminum hydride gave 6-methyl-2,3-benzocyclohepta-2,4-dienol (**16**) which was dehydrated with ethanolic hydrochloric acid to7-methyl-3,4-benzocycloheptatriene (**17**). In this case the dehydration step was more complex than for previous benzocycloheptadienols, which gave high yields of the corresponding benzocycloheptatrienes. The dehydration of **16** gave three hydrocarbon products in an approximate ratio of 50:40:10 as determined by v.p.c.



The identity of the major product as 7-methyl-3,4-benzocycloheptatriene was verified by the characteristic hydride exchange reaction with triphenylmethylcarbonium perchlorate or hexachloroantimonate to give 1-methyl-4,5-benzotropenium perchlorate or hexachloroantimonate (**18**) and triphenylmethane. The structure of this salt was verified by its n.m.r. spectrum and the similarity of its ultraviolet spectrum with that of benzotropenium perchlorate. Again, the salts of **18** showed the same characteristics as those of the ions **4** and **9**.

Addition of a solution of 1-methyl-4,5-benzotropenium perchlorate in dichloromethane to excess trimethylamine in the same solvent led to the formation of a bright yellow hydrocarbon product in *ca.* 1 hr. The structure of this hydrocarbon product as 3,4-benzoheptafulvene was established by (i) its n.m.r. spectrum (Figure 1), (ii) reconversion to 1-methyl-4,5-benzotropenium ion by trifluoroacetic acid, and (iii) its rapid hydrogenation to 5-methyl-1,2-benzocycloheptene.

Table I. N.m.r. Chemical Shifts in τ-Units Relative to Internal TMS[a]

Compd.	Benzene hydrogens	Vinyl hydrogens	Methylene hydrogens	Methyl hydrogens
3	2.80 (m)	3.50 (A part of an AB doublet, $J = 10$ c.p.s., the 5-hydrogen) 4.20 (B part of an AB doublet, $J = 10$ c.p.s., further split into triplets by the methylene hydrogens, $J = 6$ c.p.s., the 6-hydrogen) *ca.* 4.2 (the 1-hydrogen)	7.82 (t, $J = 6$ c.p.s.)	7.92 (s)
8	2.95 (m)	3.45 (A part of an AB doublet, $J = 10$ c.p.s., the 5-hydrogen) 4.12 (B part of an AB doublet, $J = 10$ c.p.s., further split into triplets, $J = 7$ c.p.s., the 6-hydrogen) *ca.* 4.1 (the 1-hydrogen)	4.20 (s, benzylic) 7.81 (t, the ring methylene hydrogens, $J = 7$ c.p.s.)	
17	2.82 (m)	3.58 (A part of an AB doublet, $J = 10$ c.p.s., further split into doublets, $J = 2$ c.p.s., the 2,5-hydrogens) 4.46 (B part of an AB doublet, $J = 10$ c.p.s., further split into doublets, $J = 7$ c.p.s., the 1,6-hydrogens)	7.65 (m)	8.82 (d, $J = 7$ c.p.s.)
6	2.8 (m)	3.2–4.3 (m)	4.98 (d, $J = 10$ c.p.s. further split into triplets, $J = 1$ c.p.s.)	
11	2.8 (m)	3–4 (m)		
19	3.04 (m)	4.01 (s)	5.28 (s)	

[a] s, singlet, d, doublet, t, triplet, m, multiplet.

Evaporation of the solvent from solutions of 3,4-benzoheptafulvene with a nitrogen stream gave a bright yellow crystalline material which was stable for short periods of time if kept under nitrogen. Thus, the three benzoheptafulvenes prepared in this study show a marked decrease in reactivity as compared to unsubstituted heptafulvene.

Comparison of the n.m.r. spectra of the benzoheptafulvenes allows assignment of some of the hydrogens, but complete assignments cannot be made for the 1,2-benzo derivatives. Integration of the n.m.r. spectrum of 1,2-benzoheptafulvene indicates that five protons lie in the aromatic region and five are in the vinyl region. The doublet at τ 4.98 integrates for one hydrogen. This hydrogen can be assigned to the 8-hydrogen *anti* to the benzene ring by comparison with the n.m.r. spectrum of 8-phenyl-1,2-benzoheptafulvene (Figure 1). Integration of this spectrum indicates ten hydrogens in the aromatic region and four hydrogens in the vinyl region. The absence of an absorption at *ca.* τ 5 corresponding to the 8-hydrogen of 1,2-benzoheptafulvene is consistent with both structural assignments. The ring current of the benzene ring would be expected to shift the *syn* hydrogen of the 8-position downfield into the aromatic region. It is to be expected that in 8-phenyl-1,2-benzoheptafulvene the phenyl will be *anti* to the benzene ring of the benzoheptafulvene and thus the hydrogen will be *syn* to the ring and shifted downfield into the aromatic region, accounting for the absence of a hydrogen absorption at *ca.* τ 5 in the n.m.r. spectrum of 8-phenyl-1,2-benzoheptafulvene. Beyond this simple analysis no further assignments can be made for the remaining hydrogens at this time.

The n.m.r. spectrum of 3,4-benzoheptafulvene is relatively simple and the peaks are readily assigned. The singlet at τ 5.28 is due to the 8-hydrogens of the heptafulvene ring system and the singlet at 4.01 is due to the 1,2,5,6-hydrogens of the heptafulvene ring. The remaining absorption at τ 3.04 is due to the benzene ring.

Based on simple HMO calculations, the predicted wave lengths for the lowest energy transitions in the ultraviolet spectra of 1,2-benzoheptafulvene and 3,4-benzoheptafulvene are 400 and 330 mμ, respectively.[18] The agreement between the observed and calculated values for 3,4-benzoheptafulvene are fortuitous since the resonance integral cannot be constant over all of the benzoheptafulvene molecule. Calculations taking into account the variation of the resonance integral would be expected to lead to more sound predictions.

From the n.m.r. data (Table I) it can be seen that the seven-membered ring hydrogens appear in the vinylic region and that there is no indication of a ring current in the seven-membered ring of the benzoheptafulvenes.

Comparison of the longest wave length electronic transitions of 1,2-benzoheptafulvene (Figure 2) and 2H-benz[*c,d*]azulene (427 mμ)[19] indicates a difference of *ca.* 100 mμ. This difference cannot be ascribed to a simple substituent effect but must be due to a substantial geometric difference between these two molecules. Molecular models indicate that in a strain-free 1,2-benzoheptafulvene the 7,8-bond is at a 90° angle to the 3,4-bond, while the same models indicate that insertion of a saturated carbon between the 8- and 9-positions of this molecule forces the seven-membered ring into coplanarity with the benzene ring. Thus, the tentative

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(18) These values are based on the resonance integral derived from the ultraviolet spectrum of heptafulvene.

(19) This data was taken from the Ph.D. Thesis of C. D. Smith, University of Oregon, 1965.

conclusion can be drawn that 1,2-benzoheptafulvene is nonplanar.

Experimental

The following analyses were performed by Alfred Bernhardt, Mulheim, Germany, and West Coast Analytical Laboratories, El Cerrito, Calif.

2-Methyl-3,4-benzocycloheptatriene. Methyl iodide (4.31 g., 0.030 mole) was added dropwise to a suspension of magnesium turnings (0.885 g., 0.364 g.-atom) in 25 ml. of anhydrous ether in a three-necked flask fitted with a reflux condenser (connected to a drying tube) and a stirrer. Addition required 20 min. 2,3-Benzocyclohepta-2,4-dienone (4.0 g., 0.025 mole; 2,4-dinitrophenylhydrazone m.p. 217–218°, lit.[12] m.p. 217°) was then added to the stirred Grignard reagent. Addition required 30 min. After the total addition of the ketone, the reaction mixture was stirred for an additional 30 min. The reaction mixture was then acidified with 100 ml. of 20% aqueous ammonium chloride. The ether layer was isolated and the aqueous solution was extracted two more times with 30 ml. of ethyl ether. The ether extract was dried over anhydrous magnesium sulfate and then concentrated on a rotary evaporator, leaving a yellow viscous oil, 3.77 g. (86.5%).

The crude methyl-2,3-benzocyclohepta-2,4-dienol (3.77 g., 0.0219 mole) was dissolved in 19 ml. of absolute ethanol. Then 19 ml. of absolute ethanol saturated with hydrochloric acid was added and the mixture was refluxed for 15 min. After cooling, the reaction solution was poured into 200 ml. of water and extracted with pentane (two 30-ml. portions). The pentane extract was dried over anhydrous magnesium sulfate and concentrated on a rotary evaporator to give a yellow liquid. The crude product was purified by chromatographing on alumina using pentane as solvent. The pentane eluate obtained was concentrated on a rotary evaporator to give a colorless liquid, 2.87 g. (84.5%). V.p.c. analysis on a DEGS column indicated that it contained two products in the ratio of 1:4.4.

Hydrogenation using prereduced Adams catalyst indicated an uptake of 1.85 moles of hydrogen. This low value and the relative v.p.c. retention times indicated that the second component is 2-methyl-3,4-benzocyclohepta-1,3-diene.

The infrared spectrum (neat, cm.$^{-1}$) showed CH, 3030 (s), 2960 (s), and 2860 (m); and C═C, 1642 (m). The ultraviolet spectrum in 95% ethanol showed 224 mμ (ϵ 36,780).

1-Methyl-2,3-benzotropenium Hexachloroantimonate. 2-Methyl-3,4-benzocycloheptatriene (0.281 g., 1.81 mmoles) dissolved in 1 ml. of dichloromethane was added to a solution of triphenylcarbonium hexachloroantimonate (1.48 g., 2.56 mmoles) in 20 ml. of dichloromethane. A green-yellow precipitate was formed within *ca.* 5 min. The product was collected on a filter and washed with dichloromethane, to give 0.541 g. (63%) of bright yellow needles, m.p. 134–135.5° dec.

Anal. Calcd. for $C_{12}H_{11}Cl_6Sb$: C, 29.42; H, 2.25. Found: C, 29.06, 29.11; H, 2.19, 2.06.

The ultraviolet spectrum (concentrated sulfuric acid) showed 425 mμ (ϵ 2275), 338 (3377), 278 (47,700), and 246 (24,600).

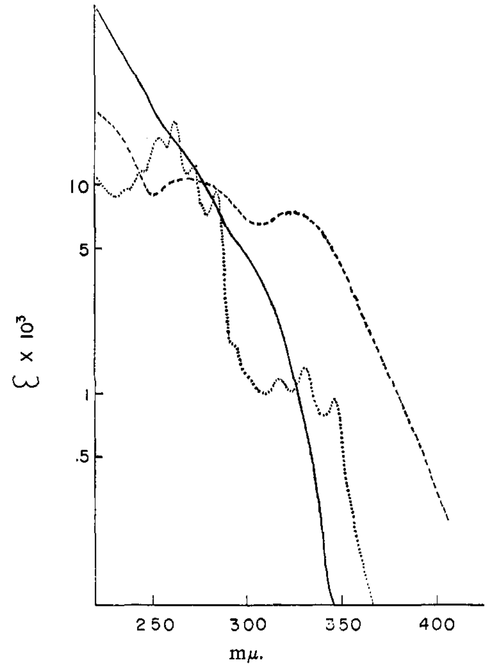

Figure 2. The ultraviolet spectra of: ......, 3,4-benzoheptafulvene; ———, 1,2-benzoheptafulvene; and – – – –, 8-phenyl-1,2-benzoheptafulvene in ether.

Triphenylmethane was recovered from the filtrate by evaporating to dryness, dissolving the residue in benzene, extracting several times with concentrated sulfuric acid, and finally by chromatographing on alumina, using petroleum ether (b.p. 60–110°) as solvent. Concentration of the eluate gave white needles, 0.255 g. (58%) of triphenylmethane, m.p. 91–92° (lit.[20] m.p. 92.5°.)

1-Methyl-2,3-benzotropenium Perchlorate. 2-Methyl-3,4-benzocycloheptatriene (0.448 g., 0.0028 mole) dissolved in 3 ml. of distilled chloroform (from P_2O_5) was added to a suspension of triphenylcarbonium perchlorate (0.985 g., 0.0028 mole) in 20 ml. of distilled chloroform. The reaction proceeded slowly and a green-yellow precipitate was formed after *ca.* 50 min. The solvent was removed with a dropper and the residue was washed two times with 5-ml. portions of distilled chloroform and finally with two 5-ml. portions of carbon tetrachloride. The n.m.r. spectrum of the salt in trifluoroacetic acid exhibited peaks at τ 0.65 (A part of an AB doublet, J = 10 c.p.s., the 4-hydrogen of the seven-membered ring), 1.03–1.83 (multiplet, the remaining benzotropenium ring hydrogens), and 6.5 (singlet, the methyl group), consistent with the structure as 1-methyl-2,3-benzotropenium perchlorate.

Triphenylmethane was recovered from the mother liquors by evaporating to dryness, dissolving the residue in benzene, extracting the benzene solution several times with concentrated sulfuric acid, and finally chromatographing on alumina, using petroleum ether (b.p. 60–90°) as solvent. Recrystallization of the crude product from ethanol gave 0.485 g. (71%) of triphenylmethane, m.p. 90–91° (lit.[20] m.p. 92.5°).

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(20) J. Schmidlin and A. Garcia Banus, *Ber.*, **45**, 3189 (1912).

1,2-Benzoheptafulvene. 1-Methyl-2,3-benzotropenium perchlorate prepared according to the preceding procedure was dissolved in 20 ml. of dichloromethane. The salt solution was then added rapidly to a solution of trimethylamine (*ca.* 5 g.) in 35 ml. of dichloromethane. The addition was made under a nitrogen atmosphere. The yellow-colored solution was capped and set aside for 16 hr. A copious, white precipitate was removed by filtration and washed with 10 ml. of dichloromethane. The filtrate was concentrated on a rotary evaporator to a semisolid. Carbon tetrachloride was quickly added to the concentrate and the yellow solution was chromatographed over alumina under a nitrogen atmosphere. The bright yellow solution was concentrated by a nitrogen stream. The yield could not be determined due to the instability of the product, which prohibited direct weighing. A solution of 1,2-benzoheptafulvene was extracted with trifluoroacetic acid. The n.m.r. spectrum of this trifluoroacetic acid solution exhibited a spectrum which was superimposable on that of 1-methyl-2,3-benzotropenium ion with an additional absorption at *ca.* τ 2.8 (accounting for *ca.* 10% of the product).

The infrared spectrum (carbon tetrachloride, cm.$^{-1}$) showed CH stretching 3030 (s) and 2940 (w); C=C stretching 1602 (s); and CH out of plane bending 888 (s) and 877 (m). The ultraviolet spectrum (ether) showed no maxima, but only a long tailing from below 210 mμ; 300 mμ (ϵ 4300) and 250 mμ (ϵ 21,800) (see Figure 2).

Hydrogenation of 1,2-Benzoheptafulvene. Ether was substituted for carbon tetrachloride in the preceding preparation. After chromatography, the eluate was diluted to 25 ml. in a volumetric flask. One milliliter of this solution was diluted and used for the ultraviolet spectrum. The remaining 24-ml. portion of the ether solution was hydrogenated at atmospheric pressure using prereduced platinum oxide. After the hydrogen uptake had ceased, the solution was filtered and concentrated to *ca.* 1 ml. by distillation through a 30-cm. Vigreux column. V.p.c. analysis of the concentrated hydrogenation product on a DEGS column indicated a single hydrocarbon product. The log ϵ plot of the ultraviolet spectrum was determined from the v.p.c. analysis. The infrared spectrum of the hydrogenation product from this v.p.c. analysis was superimposable upon that of an authentic sample of 3-methyl-1,2-benzocycloheptene derived from hydrogenation of either 2-methyl-3,4-benzocyclohepta-1,3-diene or 2-methyl-3,4-benzocycloheptatriene.

2-Methyl-3,4-benzocyclohepta-1,3-diene and 3-Methyl-1,2-benzocycloheptene. Methyl iodide (8.58 g., 0.060 mole) was added to a suspension of magnesium turnings (1.76 g., 0.072 g.-atom) in 50 ml. of anhydrous ether in a three-necked flask fitted with a reflux condenser (drying tube) and a stirrer. Addition required 50 min. 2,3-Benzocycloheptenone (7.95 g., 0.049 mole) was then added to the stirred Grignard reagent. Addition required 40 min. After total addition of the ketone, the reaction mixture was stirred for an additional 30 min. The reaction mixture was then acidified with 150 ml. of 20% aqueous ammonium chloride. The ether layer was separated and the aqueous solution was extracted with two additional 50-ml. portions of ether. After drying over anhydrous magnesium sulfate, the ether layer was evaporated on a rotary evaporator to give a yellow, viscous liquid, 6.96 g. (82%). Crude 1-methyl-2,3-benzocycloheptenol (2.0 g., 0.117 mole) was dissolved in 10 ml. of absolute ethanol and added to 10 ml. of absolute ethanol saturated with hydrochloric acid. This ethanol solution was heated to reflux for 15 min. After cooling, 50 ml. of water was added to the reaction solution and the resulting mixture was extracted with pentane. The pentane solution was concentrated on a rotary evaporator, leaving a pale yellow liquid which was chromatographed on alumina to give 1.51 g. (81%). Hydrogenation of this compound gave a hydrocarbon product the infrared spectrum of which was superimposable on that of the hydrogenation products of 2,3-benzoheptafulvene and 2-methyl-3,4-benzocycloheptatriene.

Benzyl-2,3-benzocyclohepta-2,4-dienol. Distilled benzyl chloride (8.0 g., 0.033 mole) was added slowly to a suspension of magnesium turnings (1.69 g., 0.0695 g.-atom) in 150 ml. of anhydrous ether in a three-necked flask fitted with a reflux condenser (drying tube) and a stirrer. Addition required *ca.* 40 min. Next 2,3-benzocyclohepta-2,4-dienone (5.0 g., 0.032 mole) was added to the stirred Grignard solution. Addition required about 40 min. The reaction mixture was stirred for an additional 45 min. and then acidified with 120 ml. of 20% aqueous ammonium chloride solution. The ether layer was then separated and the aqueous solution was extracted with three more portions of ether (three 50-ml. portions). The ether extract was dried over anhydrous magnesium sulfate and then concentrated on a rotary evaporator to give a light yellow liquid. The crude product was recrystallized from pentane to give white needles, 3.24 g. (41%), m.p. 66–68°.

Anal. Calcd. for $C_{18}H_{18}O$: C, 86.36; H, 7.24. Found: C, 86.01; H, 7.38.

2-Benzyl-3,4-benzocycloheptatriene. 1-Benzyl-2,3-benzocyclohepta-2,4-dienol (2.38 g., 0.0096 mole) was dissolved in 10 ml. of anhydrous ethanol and added to 10 ml. of a solution of ethanol saturated with hydrochloric acid. The resulting solution was refluxed for 20 min. After cooling, the reaction solution was poured into 150 ml. of water and then extracted with two 30-ml. portions of pentane. The pentane extract was dried over anhydrous magnesium sulfate and then concentrated on a rotary evaporator to give a yellow liquid. The crude product was chromatographed on alumina using pentane as solvent. The eluate was then concentrated on a rotary evaporator to give a colorless liquid, 1.64 g. (69%). Hydrogenation using prereduced platinum oxide indicated an uptake of 1.80 moles of hydrogen.

The infrared spectrum (neat, cm.$^{-1}$) showed CH, 3000 (s), 2940 (m), 2900 (m), and 2820 (w); and C=C, 1634 (w). The ultraviolet spectrum (95% ethanol) showed 223 mμ (ϵ 41,100).

1-Benzyl-2,3-benzotropenium Hexachloroantimonate. 2-Benzyl-3,4-benzocycloheptatriene (0.175 g., 0.76 mmole) dissolved in 1 ml. of dichloromethane was added to a solution of triphenylcarbonium hexachloroantimonate (0.44 g., 0.76 mmole) in 10 ml. of dichloromethane. After *ca.* 10 min. some of the solvent was evaporated off by a nitrogen stream and 3 ml. of distilled chloroform was added, causing a green-yellow precipitate to form. The product was collected on a filter and washed with 2 ml. of dichloromethane and finally with a few milliliters of chloroform to give 0.267 g. (61%) of bright yellow needles, m.p. 108–109° dec.

Anal. Calcd. for $C_{18}H_{15}Cl_6Sb$: C, 38.21; H, 2.65. Found: C, 37.98, 37.84; H, 2.66, 2.75.

The ultraviolet spectrum (concentrated sulfuric acid) showed 435 mμ (ϵ 3560) 342 (4274), 284 (46,900), 246 (34,600), and 227 (30,400).

Triphenylmethane was recovered from the filtrate by evaporating to dryness, dissolving the residue in benzene, extracting the benzene solution several times with concentrated sulfuric acid, and finally evaporating off the solvent. The crude product was chromatographed on alumina, using pentane as solvent. Concentration of the eluate gave 60 mg. (41%) of triphenylmethane, m.p. 91–92° (lit.[20] m.p. 92.5°).

1-Benzyl-2,3-benzotropenium Perchlorate. 2-Benzyl-3,4-benzocycloheptatriene (0.445 g., 1.9 mmoles) dissolved in 2 ml. of distilled chloroform (from P_2O_5) was added to a suspension of triphenylcarbonium perchlorate (0.855 g., 1.9 mmoles) in 20 ml. of distilled chloroform. A brown oil was formed in *ca.* 30 min. The solvent was then removed with a dropper and the product was washed with 5 ml. of chloroform and finally with 5 ml. of carbon tetrachloride. The residue, which was a brown oil, was then dissolved in trifluoroacetic acid. The n.m.r. spectrum of this perchlorate salt showed peaks at τ 0.25 (A part of an AB doublet, J = 10 c.p.s., the 4-hydrogen of the seven-membered ring), 0.5–1.55 (multiplet, the remaining benzotropenium ring hydrogens), 2.67 (singlet, the hydrogens of the phenyl ring), and 4.72 (singlet, the benzylic methylene hydrogens), which was consistent with the assigned structure. Because of the tendency for this compound to form an oil, it was difficult to remove the last traces of unreacted triphenylcarbonium perchlorate. For this reason the n.m.r. samples usually exhibited a few per cent of this ion. However, the two ions could readily be resolved in the n.m.r. spectrum.

Triphenylmethane was recovered from the extract by concentration to a solid residue. The residue was purified by dissolving in benzene, extracting several times with concentrated sulfuric acid, concentration, and finally chromatography on alumina using pentane as solvent. Evaporation of the solvent gave triphenylmethane, 326 mg. (70%), m.p. 90–91° (lit.[20] 92.5°).

8-Phenyl-1,2-benzoheptafulvene. 2-Benzyl-3,4-benzocycloheptatriene (0.765 g., 3.30 mmoles) dissolved in 5 ml. of distilled chloroform (from P_2O_5) was added to a solution of triphenylcarbonium perchlorate (1.14 g., 3.30 mmoles) in 25 ml. of distilled chloroform. The reaction proceeded slowly with a brown oil forming after about 30 min. After 1 hr. the solvent was removed with a dropper and the residue was washed two times with 5-ml. portions of distilled chloroform. The residual oil was dissolved in 20 ml. of dichloromethane and the resulting solution was added rapidly to a solution of 7 ml. of trimethylamine in 40 ml. of dichloromethane. The reaction mixture was allowed to stand at room temperature for 16 hr. A copious white precipitate was removed by filtration and washed with 10 ml. of dichloromethane. This filtrate was concentrated on a rotary evaporator and carbon tetrachloride was immediately added to the semisolid residue. The resulting solution was then chromatographed over alumina, under a nitrogen atmosphere. The bright yellow eluate was concentrated by a nitrogen stream. Extraction of a solution of 8-phenyl-1,2-benzoheptafulvene with trifluoroacetic acid and determination of the n.m.r. spectrum gave a spectrum identical with that of 1-benzyl-2,3-benzotropenium ion.

The infrared spectrum (carbon tetrachloride, $cm.^{-1}$) showed CH, 3030 (s), 2940 (m), and 2870 (w); C=C, 1602; and CH out of plane bending, 815 (m). The ultraviolet spectrum (anhydrous ether) showed 321 mμ (ϵ 7580) and 267 mμ (ϵ 11,180).

Hydrogenation of 8-Phenyl-1,2-benzoheptafulvene. A solution of 8-phenyl-1,2-benzoheptafulvene in anhydrous ether was used for hydrogenation. Ether was substituted for carbon tetrachloride in the preceding preparation. This ether solution was hydrogenated at atmospheric pressure with prereduced platinum oxide. After the hydrogen uptake had ceased, the solution was filtered and concentrated to *ca.* 1 ml. by distillation through a 30-cm. Vigreux column. The residue was then evacuated to 1 mm. for 30 min. to remove the residual ether. The infrared spectrum of this hydrogenation product was superimposable upon an authentic sample of 3-benzyl-1,2-benzocycloheptene derived from hydrogenation of 2-benzyl-3,4-benzocycloheptatriene.

3-Methyl-4-benzoylbutanoic Acid. A solution of 3-methylglutaric anhydride (100 g., 0.87 mole) in 90 ml. of benzene was added dropwise to a stirred suspension of aluminum chloride (258 g., 1.94 moles) in 400 ml. of benzene. The reaction mixture was kept cooled in an ice bath during the addition of the anhydride, which required 50 min. The red-orange reaction mixture was warmed to room temperature and stirred for 1 additional hr. Finally the reaction mixture was added to a mixture of 80 ml. of concentrated hydrochloric acid and 500 g. of ice, giving a white precipitate. The product was collected on a filter and washed thoroughly with water and dried to give 149 g. (89%) of crude product. Two recrystallizations from benzene–petroleum ether gave white needles, m.p. 77.5–79°.

Anal. Calcd. for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 70.00; H, 6.88.

3-Methyl-5-phenylpentanoic Acid. 3-Methyl-4-benzoylbutanoic acid (102 g., 0.50 mole), 85% hydrazene hydrate (68 ml.), and potassium hydroxide (94 g., 1.43 moles) were dissolved in 650 ml. of ethylene glycol and refluxed for 1 hr. The reaction mixture was then distilled until the temperature in the flask reached 205–207°. Distillation was then stopped and the reaction mixture was refluxed for an additional 3 hr. The cooled reaction mixture was added to a solution of 266 ml. of concentrated hydrochloric acid in 825 ml. of water. The acidified mixture was then extracted with three 100-ml. portions of ether and the ether solution was concentrated on a steam bath to give a pink, viscous oil, 76 g. (80%) (anilide m.p. 109–110.5°).

Anal. Calcd. for $C_{18}H_{21}NO$: C, 80.86; H, 7.92. Found: C, 80.88; H, 7.97.

6-Methyl-2,3-benzocyclohept-2-enone. Crude 3-methyl-5-phenylpentanoic acid (74.6 g., 0.38 mole) was dissolved in 770 g. of polyphosphoric acid. The mixture was heated, with stirring, in a water bath to 93–95° for 5 min. The brown reaction mixture was then poured into a mixture of 300 g. of ice and 500 ml. of water. The resulting yellow mixture was extracted with three 100-ml. portions of ether. The ether solution was washed with aqueous sodium bicarbonate until the aqueous layer remained basic, and then with water. Concentration of the dried ether extract on a rotary evaporator gave a brown, viscous oil. Distillation of the crude product gave a colorless liquid, 45.4 g. (67%), b.p. 109–111° (1 mm.) (2,4-dinitrophenylhydrazone m.p. 210–212°).

Anal. Calcd. for $C_{18}H_{18}N_4O_4$: C, 61.01; H, 5.12. Found: C, 61.00; H, 5.18.

6-Methyl-2,3-benzocyclohepta-2,4-dienone. A solution of 6-methyl-2,3-benzocyclohept-2-enone (10.0 g., 0.057 mole) and azobisisobutyronitrile (0.1 g.) in 200 ml. of carbon tetrachloride was added to N-bromosuccinimide (10.3 g., 0.63 mole) and the resulting suspension was refluxed for 45 min. The reaction mixture was then cooled and filtered to remove the succinimide. Concentration of the filtrate on a rotary evaporator gave a yellow, viscous oil. This crude 4-bromo-6-methyl-2,3-benzocyclohept-2-enone was then dissolved in 300 ml. of dimethylformamide and 2.0 g. of magnesium hydrogen phosphate was added. The resulting mixture was then heated to 80°, while stirring under nitrogen, for 28 hr. The reaction mixture was then added to 500 ml. of water and extracted with ether (three 100-ml. portions). The ether extract was then concentrated on a rotary evaporator to give a brown, viscous oil. Distillation of the crude product gave 5.6 g. (56%) of a light yellow liquid, b.p. 116–118° (2 mm.) (2,4-dinitrophenylhydrazone m.p. 213–214° (a mixture melting point with the 2,4-dinitrophenylhydrazone of 6-methyl-2,3-benzocyclohept-2-enone gave a 18° depression)).

Anal. Calcd. for $C_{18}H_{16}N_4O_4$: C, 61.35; H, 4.58. Found: C, 60.95; H, 4.72.

V.p.c. analysis of the distilled product on a DEGS column showed two peaks in the ratio of 1:3. The n.m.r. spectrum of the smaller portion was identical with that of 6-methyl-2,3-benzocyclohept-2-enone. The n.m.r. spectrum of the larger portion was consistent with the assigned structure as 6-methyl-2,3-benzocyclohepta-2,4-dienone.

6-Methyl-2,3-benzocyclohepta-2,4-dienol. A solution of 6-methyl-2,3-benzocyclohepta-2,4-dienone (1.25 g., 0.72 mmole) in 2 ml. of ether was added to a stirred suspension of lithium aluminum hydride in 20 ml. of ether. The resulting solution was allowed to stir an additional 30 min. and then was acidified with 50 ml. of 20% aqueous ammonium chloride. The ether layer was separated and the aqueous layer was extracted with two additional 20-ml. portions of ether. Evaporation of the solvent on a rotary evaporator gave white crystals, 1.06 g. (84%). Recrystallization from pentane gave white needles, m.p. 81–82°.

Anal. Calcd. for $C_{12}H_{14}O$: C, 82.72; H, 8.09. Found: C, 82.50; H, 7.92.

7-Methyl-3,4-benzocycloheptatriene. A solution of 6-methyl-2,3-benzocyclohepta-2,4-dienol (1.96 g., 0.0113 mole) in 10 ml. of anhydrous ethanol was added to 10 ml. of anhydrous ethanol saturated with hydrochloric acid and refluxed for 45 min. The resulting yellow solution was cooled and added to 50 ml. of water. The resulting mixture was then extracted with three 20-ml. portions of pentane. The pentane solution was concentrated on a rotary evaporator to a yellow liquid. The crude product was chromatographed over alumina and the eluate was concentrated on a rotary evaporator to give a colorless liquid, 1.47 g. (83%). V.p.c. analysis of this liquid showed three components in a ratio of 50:40:10. The n.m.r. spectrum indicated that the most abundant component was 7-methyl-3,4-benzocycloheptatriene.

1-Methyl-4,5-benzotropenium Hexachloroantimonate. Crude 7-methyl-3,4-benzocycloheptatriene (300 mg., 1.93 mmoles), dissolved in 5 ml. of dichloromethane, was added to a solution of triphenylcarbonium hexachloroantimonate (1.10 g., 1.93 mmoles) in 20 ml. of dichloromethane. A yellow precipitate was formed within 1 min. The product was collected on a filter and washed with dichloromethane to give 498 mg. (51%) of bright yellow needles m.p. 124–125° dec.

Anal. Calcd. for $C_{12}H_{11}Cl_6Sb$: C, 29.42; H, 2.25. Found: C, 29.37, 29.38; H, 2.54, 2.48.

The ultraviolet spectrum (concentrated sulfuric acid) showed 415 mμ (ϵ 2340), 354 (3990), 340 (4910), and 285 (103,800).

Triphenylmethane was recovered from the filtrate by evaporating to dryness, dissolving the residue in benzene, extracting the benzene solution several times with concentrated sulfuric acid, and chromatographing over alumina using pentane as solvent. Recrystallization of the chromatographed product from ethanol gave 227 mg. (47%) of triphenylmethane, m.p. 91–92° (lit.[20] m.p. 92.5°).

1-Methyl-4,5-benzotropenium Perchlorate. A solution of 7-methyl-3,4-benzocycloheptatriene (475 mg., 3.04 mmoles) dissolved in 2 ml. of distilled chloroform (from P_2O_5) was added to a suspension of triphenylcarbonium perchlorate (833 mg., 2.43 mmoles) in 15 ml. of distilled chloroform. A green-yellow precipitate started to form after about 10 min. The reaction mixture was allowed to stand under nitrogen for 2 hr. The solvent was then removed with a dropper and the residue was washed twice with 5-ml. portions of chloroform. The n.m.r. spectrum of the product in trifluoroacetic acid exhibited peaks at τ 0.44 (A part of an AB doublet, $J = 11$ c.p.s., the 3,6-hydrogens of the seven-membered ring), 0.84 (multiplet, the remaining ring hydrogens), and 6.67 (singlet, the methyl hydrogens). This spectrum was consistent with the assigned structure.

Triphenylmethane was recovered from the extract by evaporating the solvent, dissolving the residue in benzene, extracting several times with concentrated sulfuric acid, and finally chromatography on alumina using pentane as solvent. Recrystallization from ethanol gave 303 mg. (41%) of triphenylmethane, m.p. 91–92° (lit.[20] m.p. 92.5°).

3,4-Benzoheptafulvene. 1-Methyl-4,5-benzotropenium perchlorate, prepared according to the preceding procedure, was dissolved in 20 ml. of dichloromethane and added rapidly to a solution of trimethylamine (5 ml.) in 30 ml. of dichloromethane. A precipitate started to form in a few minutes. After 30 min. the trimethylammonium perchlorate (43%) was collected on a filter. The infrared spectrum of this salt was identical with that of an authentic sample of trimethylammonium perchlorate. After another hour the filtrate was concentrated on a rotary evaporator and the residue was dissolved quickly in carbon tetrachloride. The yellow solution was then chromatographed on alumina under a nitrogen atmosphere. Evaporation of the eluate by a nitrogen stream left bright yellow needles which were stable for short periods if kept in a nitrogen atmosphere. Extraction of a carbon tetrachloride solution of 3,4-benzoheptafulvene with trifluoroacetic acid and determination of the n.m.r. spectrum gave a spectrum that was identical with that of 1-methyl-4,5-benzotropenium ion.

The infrared spectrum (carbon tetrachloride, cm.$^{-1}$) showed CH, 3030 (s) and 3060 (s); C=C, 1560; and CH out of plane bending, 858 (s). The ultraviolet spectrum (ether) showed 345 mμ (ϵ 965), 328 (1430), 296 sh (1495), 281 (9360), 271 (12,400), 261 (19,800), 252 (16,500), 245 sh (11,650) and 237 sh (9250).

Hydrogenation of 3,4-Benzoheptafulvene. Ether was substituted for carbon tetrachloride in the preceding preparation. After chromatographing, the eluate was concentrated by nitrogen, and the ether solution was hydrogenated with prereduced platinum oxide catalyst. The infrared spectrum of the hydrogenation product was identical with that of an authentic sample of 5-methyl-1,2-benzocycloheptene derived from 5-methyl-1,2-benzocyclohepta-1,3-diene.

5-Methyl-1,2-benzocyclohepta-1,3-diene. A solution of 6-methyl-2,3-benzocyclohept-2-enone (0.872 g., 0.05 mole) in anhydrous ether was added to a suspension of lithium aluminum hydride (0.19 g., 0.05 mole) in ether. The reaction required 30 min. The reaction mixture was then acidified with 80 ml. of 20% aqueous ammonium chloride. The ether layer was separated and the aqueous layer was further extracted with two 50-ml. portions of ether. The ether extract was then dried over anhydrous potassium carbonate. Concentration of the ether solution gave white crystals. Recrystallization from ethanol–water gave 0.73 g. (84%), of white needles, m.p. 135–137°. 6-Methyl-2,3-benzocycloheptenol (0.46 g., 0.026 mole) was dissolved in 5 ml. of absolute ethanol. Then 5 ml. of ethanol saturated with hydrochloric acid was added and the reaction mixture was refluxed for 20 min. After this period the reaction mixture was poured into 80 ml. of water and extracted with pentane. The pentane extract was dried over anhydrous magnesium sulfate and the solvent was removed on a rotary evaporator. The crude product was chromatographed on alumina giving 0.37 g. (80%) of 5-methyl-1,2-benzocyclohepta-1,3-diene. This material was hydrogenated on prereduced platinum oxide to give 5-methyl-1,2-benzocycloheptene.

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Steroids. CCLXXIII.[1] The Chemistry of Some Norcaradiene and Cycloheptatriene Analogs[2,3]

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Reaction of 19-hydroxyandrost-4-ene-3,17-dione (**2a**) *with 2-chloro-1,1,2-trifluorotriethylamine* (**1**) *affords two 5,19-cyclo steroids,* **3a** *and* **4a**. *Both products are converted by methanolic hydrochloric acid to 5β-chloromethylestrane-3,17-dione* (**8**). *Proofs of structure and further chemical transformations are described. Several steroidal cycloheptatrienes have been prepared and their properties are discussed in relation to the cycloheptatriene–norcaradiene isomerism. Removal of fluorine from nonallylic tertiary carbon by prolonged exposure to lithium aluminum hydride is reported.*

Persistent interest in methods of fluorinating alicyclic compounds led to an extensive survey of the reactions of 2-chloro-1,1,2-trifluorotriethylamine (**1**)[4] with steroidal alcohols.[5,6] Reaction led typically to fluoro steroids, chlorofluoracetate esters, and dehydration products, often following skeletal carbon–carbon bond migration as an intermediate step. Occasionally solvent intervention in the reaction was observed. The broad range of products was consistent with generation of an incipient carbonium ion followed by collapse along well-precedented paths.[5] A remarkable, and at first capricious, dependence of product composition upon the reaction conditions, especially the nature of the solvent, and the work-up procedure was observed.[7]

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(7) Successful solutions to these problems have been applied recently in the synthesis of 19-nor-7-fluoro-B-homosteroids: L. H. Knox, E. Velarde, S. Berger, I. Delfin, R. Grezemkovsky, and A. D. Cross, to be published.